



Fig. 1 Previous developments concerning electrochemical transformations of organosilicons.

at a forefront of such a policy, by setting the stage for molecular synthesis with unique levels of resource economy (e.g., chemicals, wastes, energy, etc.).⁶⁴ The cathodic reduction, indeed, benefits from readily available chlorosilanes and the absence of additional mediators. However, the anodic oxidation process requires additional mediators, the use of limited hydrosilanes or their precursors. Nevertheless, novel electro-mediated methodologies seem to lead to fascinating new reactions, whereas the full potential of paired electro-synthetic approaches will hopefully be uncovered in the near future.²²

This short perspective will mainly focus on the recent developments in the electrochemical synthesis of organosilicon compounds. It aims to explain the significance of these developments, provide a critical look at this subject, and identify further challenges. Five recent articles (2020–2022) were selected and the features of these solutions will be discussed with an appropriate description of mechanistic studies and their usefulness.

In 2020, Lin and coworkers described the synthesis of a wide range of organosilicon compounds *via* electro-synthesis.⁶⁵ For the disilylation of alkenes (Fig. 3), the authors used the following combination: Mg anode (sacrificial), graphite cathode, CCE @ 10 mA, and TBAClO₄ as the electrolyte.

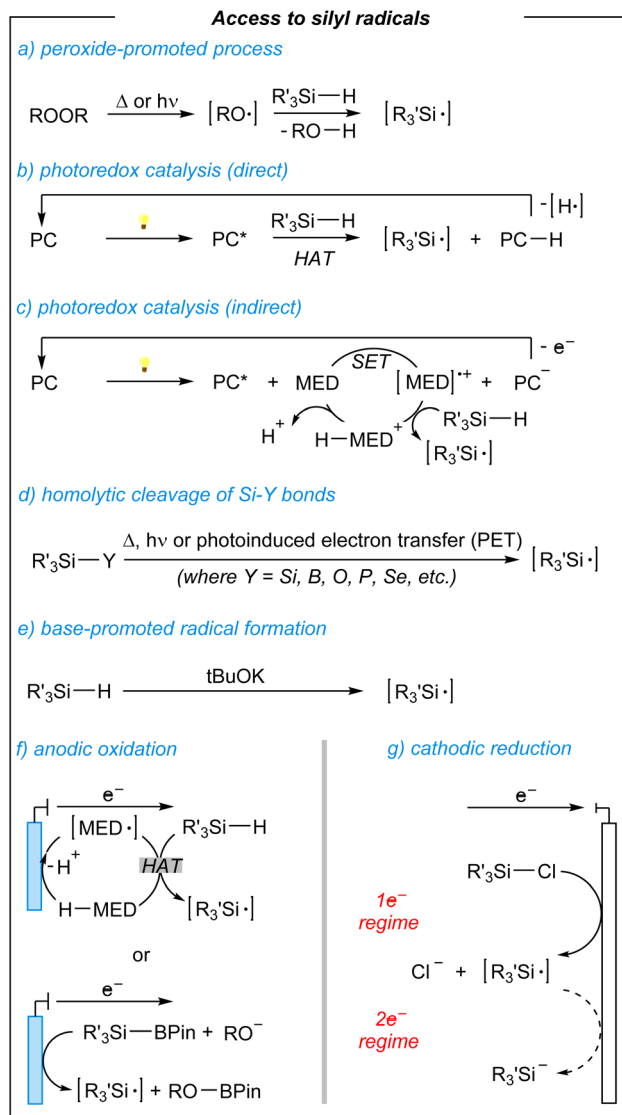


Fig. 2 Overview of general ways for the generation of silyl radicals.

Upon the investigation of the reaction scope, several styrenes, vinylboronates, and vinyl-N-heterocycles were efficiently disilylated at rt, in moderate to very good yields (45–93%). Moreover, the authors performed analogues digermylation, and used other chlorosilanes than chlorotrimethylsilane such as chlorodimethylsilane, chloropentamethyldisilane and chlorotriethylsilane. Among the unreactive or less reactive (and less selective) reagents, one can mention β-methylstyrene, styrenes with strong electron-withdrawing groups, 3-vinylpyridine, allylbenzene, cyclooctene (alkene substrates), as well as dichlorosilanes, chlorotert-butyl dimethylsilane and chlorodimethylphenylsilane (chlorosilanes). Meanwhile, a silyl radical pathway was proposed. The authors conducted detailed mechanistic studies by performing several electroanalytical experiments. The reaction system involved three species that could be reduced at the cathode – chlorosilane, alkene, and magnesium cation (Mg²⁺). The last one was excluded since





Fig. 3 Disilylation of alkenes *via* electroreductive activation.

magnesium (Mg^0 , electrogenerated or as a powder) gave no product under the optimized conditions. Moreover, the electrolysis performed in a divided cell led to the desired product. Then, cyclic voltammetry experiments suggested the reduction of chlorosilane prior to the alkene. The plausible mechanism is depicted in Fig. 4.

Next, considering the plausible mechanism of this electroreductive process, the authors envisaged a completely novel methodology for the formation of silacycles (Fig. 5). Thus, several tethered silanes including dichlorodi-, tri- and tetrasilanes, as well as dichlorodisiloxane and 1,2-bis(chlorodimethylsilyl)ethane were utilized as the substrates under the same conditions. As the result, seven new silacycles (five- and

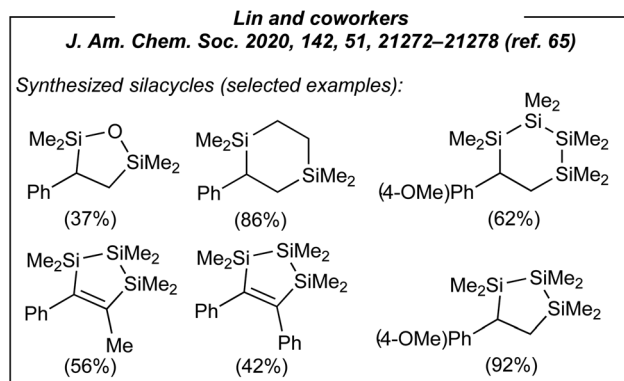


Fig. 5 Selected silacycles obtained *via* electroinduced disilylation of alkenes with tethered dichlorosilyl derivative.

six-membered ones) were obtained in good yields up to 92%. Subsequently, the authors again showed how important is to understand the nature of the process. After the synthesis of the above-mentioned silacycles, the portfolio of the products was extended to monosilylated alkanes (*via* formal hydrosilylation) and allylsilanes. In the case of the former, acetonitrile was used as both solvent and the hydrogen source (Fig. 6). In the latter case, the introduction of a leaving group in β -position to the carbanion intermediate was required.

Finally, Lin demonstrated the derivatization of the obtained organosilicon products to a variety of structurally diverse compounds *via* known transformations including fluorination, oxidation, and Fleming–Tamao oxidation.⁶⁶

To sum up, Lin and coworkers reported a novel methodology for the construction of sp^3 C–Si moieties, induced by electricity. Firstly, they used chlorosilanes. This group of silicon compounds is the most numerous on the commercial

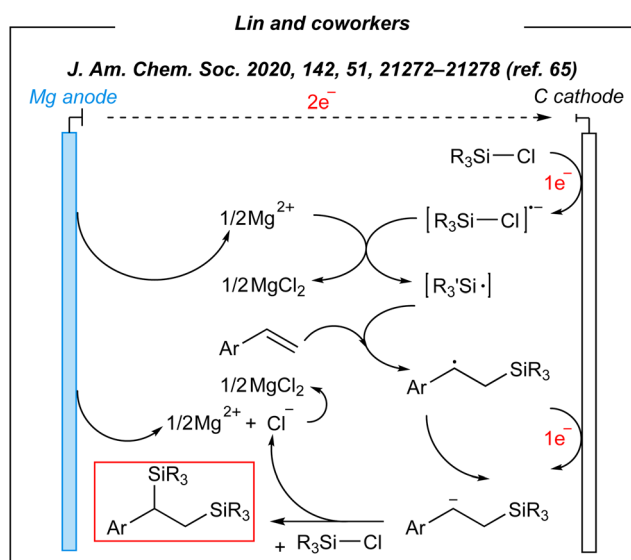


Fig. 4 Plausible mechanism for the disilylation of alkenes under electrochemical conditions.



Fig. 6 Hydrosilylation of alkenes *via* electroreductive activation.



market, thus their prices are typically lower than corresponding hydrosilanes. Of the major drawbacks should be noted moisture sensitivity and corrosive character of SiCl-containing derivatives. And all this implies the necessity for an inert atmosphere during the process. Moreover, the authors used tetrabutylammonium perchlorate (TBAClO₄) as the electrolyte. This is a strong oxidizer, which is potentially explosive.^{67,68} However, a more user-friendly electrolyte such as tetrabutylammonium bis(trifluoromethanesulfonyl)imide (TBATFSI) can also be utilized giving only slightly inferior conversion. The electrochemical system consists of an anode (Mg) and graphite cathode (carbon-based electrodes are typically inexpensive). Whilst the former one is sacrificial, extended reaction time and delivered charge can lead to the deposition of combustible Mg⁰ layer on the cathode surface. Next, the authors used standardized IKA® equipment. This is a commercialized setup, which gives an appropriate level of reproducibility. This is a very important aspect, whereas the electrode arrangement can lead to different efficiencies. Finally, the novelty and significance of this approach will be evaluated. This is a novel methodology giving a wide range of fascinating insights. It may lead to further developments in the field. Furthermore, hitherto methodologies leading to the same products were limited. In the case of disilylation reaction, previous methods were mainly based on the use of strong reducing agents,⁶⁹ expensive Pt/Pd catalysts,^{70–75} or silylium-ion catalysis.^{76,77} The latter one, despite its high scientific significance, is still in its infancy and in this particular case is mostly limited to one disilane (hexamethyldisilane). The Lin group showed also the possibility to perform transition metal-free hydrosilylation using chlorosilanes (however, it should be noted that preparation of carbon electrodes may introduce traces of metal impurities⁷⁸). In the vast majority of cases, the hydrosilylation of unsaturated bonds requires the use of more expensive hydrosilanes, and radical initiators or transition metal complexes (mostly Pt or Ru).^{34,79–82} Thus, the utilization of chlorosilanes instead of hydrosilanes or (limited in number) transfer hydrosilylation agents⁸³ seems to be an intriguing idea. There were only two examples, where chlorosilanes were used to give formal hydrosilylation products (magnesium-promoted reductive silylation reported by Maekawa⁸⁴ and electrochemically-induced silylation of styrenes by Jouikov⁸⁵). In conclusion, the electrochemical disilylation reported by Lin and coworkers is a sustainable alternative to conventional stoichiometric or catalytic methods, and despite some limitations in scope (*e.g.*, mostly an introduction of alkylsilyl group), it can be considered as useful synthetic approach.

In 2021, Zhang and coworkers described the synthesis of a wide range of organosilanols *via* electro-synthesis.⁸⁶ For the hydrolysis of hydrosilanes (Fig. 7), the authors used the following combination: RVC anode (RVC = reticulated vitreous carbon), nickel foam cathode, CCE @ 12 mA, and *n*Bu₄NPF₆ as the electrolyte. During the optimization studies, several HAT mediators were tested including NHPI (selected, *N*-hydroxyphthalimide), NHSI (*N*-hydroxysuccinimide), TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl], and DABCO (1,4-dia-

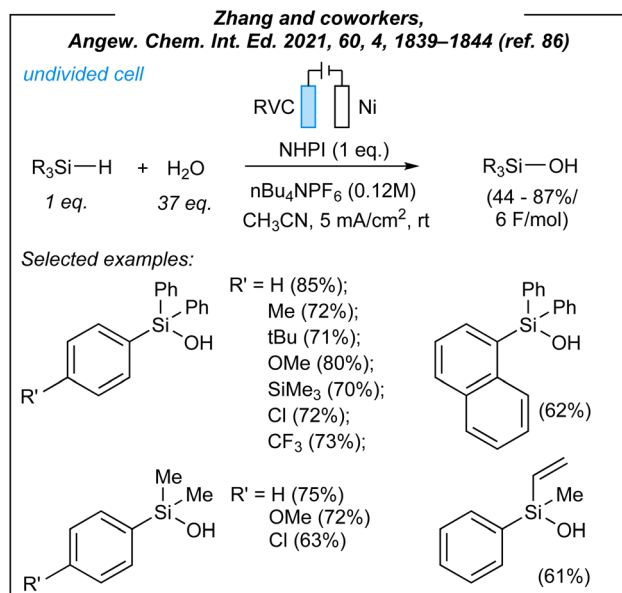


Fig. 7 Silanol-oriented hydrolysis of hydrosilanes under electrochemical conditions.

zabicyclo[2.2.2]octane). The mediator-free attempt was also carried out and proved the essential role of the HAT-step. Next, the authors explored the substrate scope concerning several hydrosilanes. A wide range of triphenylsilyl derivatives worked efficiently under the reaction conditions, as well as naphthyl-, alkyl-, alkenyl-, alkynyl-, and heteroaryl-substituted substrates. Moreover, the synthetically useful dihydro derivatives such as 1,4-bis(diphenylsilyl)benzene and diphenylsilyl were also well tolerated, and led to their silanol analogues in moderate yields (56% and 62%, respectively).

Encouraged by these results, Zhang investigated also the use of silyl-derived natural products and drugs, which are bio-relevant scaffolds (Fig. 8). All of them afforded the expected products in moderate to good yields (44–78%).

Furthermore, the authors replaced water with alcohol to check the possible alcoholysis of hydrosilanes under electrochemical conditions. Using quinuclidine as the HAT mediator (3.0 eq.), the alcohols including methanol, 1-adamantanol, 1-menthol, and (–)-nopol provided four silyl ethers in moderate to very good yields (51–89%).

To gain some mechanistic insights into this electroinduced transformation, the authors conducted several electrochemical experiments. The reaction system involved a HAT mediator – NHPI, which undergoes an anodic oxidation process facilitated by cathodically-generated hydroxides. As the result, the PINO radical (phthalimide *N*-oxyl) is afforded and it abstracts the hydrogen atom from the Si–H bond of hydrosilanes. The formed silyl radicals are subsequently oxidized to silyl cations. The formed R₃Si⁺ species are instantaneously trapped by O-nucleophiles (hydroxide anion or water can quench the cation, but an excess of water favors the latter one) to give the corresponding silanols. It is worth noting that other mediums such



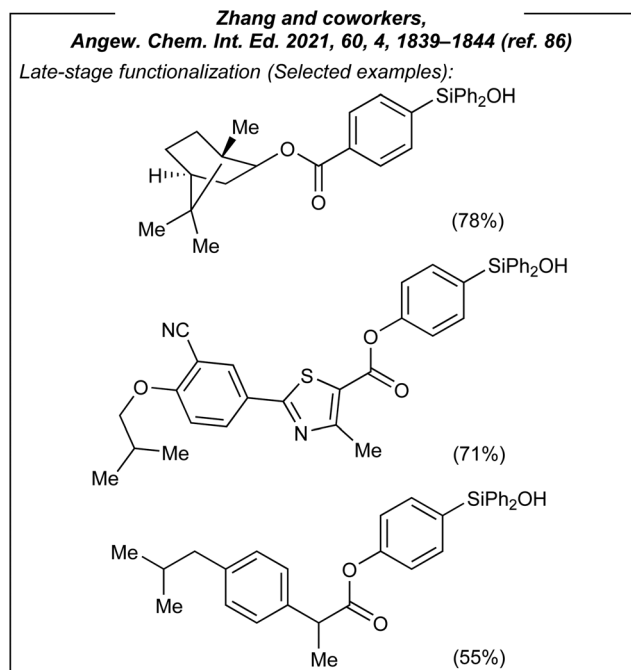


Fig. 8 Selected biorelevant compounds obtained *via* electroinduced hydrolysis of Si–H bonds.

as dichloromethane and dimethylformamide were ineffective solvents in this process, whilst acetonitrile, known for stabilizing silyl cations,⁸⁷ ensured the best conversion. The plausible mechanism is depicted in Fig. 9.



Fig. 9 Plausible mechanism for the hydrolysis of hydrosilanes under electrochemical conditions.

To sum up, Zhang and coworkers reported a novel methodology for the construction of O–Si moieties, induced by electricity. First of all, the authors used hydrosilanes as the substrates. Unlike chlorosilanes, SiH-containing molecules are less sensitive and lead to non-corrosive byproducts. However, they are not as readily available as halosilanes, which serve as the first-choice substrates in conventional methods.⁸⁸ Indeed, chlorosilanes readily undergo hydrolysis to give corrosive HCl (usually trapped by amine bases) and silanols. Unfortunately, the chemoselectivity of these transformations is generally low, whereas silanols can easily undergo condensation to disiloxanes. Zhang's approach gives access to both types of silanols, these easily available from chlorosilanes (*e.g.*, triisopropylsilanol), and those difficult to be conventionally produced with good selectivity (*e.g.*, SiMe₂-containing silanols). What is more, the authors performed the challenging hydrolysis of silyl-derived biorelevant compounds, which contain sensitive functional groups. Furthermore, in the vast majority of cases, the conversion of Si–H to Si–OH moieties requires the use of stoichiometric oxidants and/or expensive transition metal catalysts.^{39,89} Thus, the electrochemical approach seems to be a very significant alternative to known procedures utilizing hydrosilanes as the substrates. The authors performed also pioneering alcoholysis reactions leading to alkoxy silanes under electrochemical conditions. In the past, several sustainable methods were developed,^{39,90–93} but this electroinduced approach might be interesting in the case of the compounds with sensitive groups. Furthermore, the electrochemical system consists of an RVC anode and a nickel cathode. Both are classified as not so expensive. Similarly to Lin,⁶⁵ the Zhang group used an IKA® ElectraSyn 2.0, which ensures the reproducibility of the obtained results. In addition, what is equally important, the authors tested the reaction under electricity-free (as well as mediator-free and catalyst-free) conditions to show the necessity of electroinduced synthesis. This is a very important aspect, whereas some processes can be performed *via* uncatalyzed reactions or without additional terms and conditions.^{94–96} In conclusion, the electrochemical hydrolysis reported by Zhang and coworkers is an interesting alternative to conventional stoichiometric or catalytic methods, and despite some limitations (*e.g.*, stoichiometric amounts of HAT mediator, moderate yields, *etc.*), it can be considered as a useful synthetic approach.

In 2021, He and coworkers reported the radical 1,2-silyl-functionalization of alkenes under electrochemical conditions.⁹⁷ For the silyl-oxygenation process (Fig. 10), the authors used the following combination: graphite anode, platinum cathode, CCE @ 3 mA, NHPI as HAT mediator (1.2 eq.), and LiClO₄ as the electrolyte. Upon the investigation of the reaction scope, several hydrosilanes (including secondary and tertiary ones) were matched with electron-deficient alkenes and different *N*-oxyl species. In most cases, that was a combination of triphenylsilanes, acrylonitrile, and NHPI. As the result, several β-silyl-cyanohydrines were obtained with moderate to good yields. Moreover, He demonstrated that acrylates, vinyl phenyl sulfone, and vinyl phenyl ketone are also suitable





Fig. 10 Radical 1,2-silylfunctionalization of alkenes under electrochemical conditions.

alkene partners, whilst styrene and vinyl ether more or less gave no product. Furthermore, tertiary and secondary germanes were also reactive under these electrochemical conditions, giving β -germyl-cyanohydrins in moderate yields (33–60%). Finally, the described protocol was scaled up to a 5 mmol scale yielding 72% (1.71 g) of 2-((1,3-dioxoisindolin-2-yl)oxy)-3-(triphenylsilyl)propanenitrile. This once again makes it clear that the proposed methodology has significant application potential. Next, the authors demonstrated the derivatization of the obtained β -silyl-cyanohydrins to a variety of structurally diverse compounds *via* transformations of all three functional groups found in the mentioned scaffold.

Thus, it was shown that Si–H group can be efficiently converted to Si–OH moiety in the presence of oxidant and rhenium catalyst (however, it would be interesting to check previously mentioned Zhang's electrochemical conditions to perform this reaction under catalyst-free and external oxidant-free conditions). Moreover, it was demonstrated that nitrile as well as *N*-oxyl groups can be efficiently transformed into other functions such as tetrazoles and α -aminoxy derivatives respectively.

To gain mechanistic insights into these electroinduced reactions, the authors conducted some preliminary experiments and suggested a plausible mechanism (Fig. 11). A radical clock experiment was carried out giving the ring-opening product in 28% yield. This experiment implied that the radical pathway is operative. It is well-known the direct anodic oxidation of hydrosilanes is very difficult due to the high redox potential of Si–H bonds. The CV studies confirmed these presumptions, showing that oxidation of NHPI to PINO

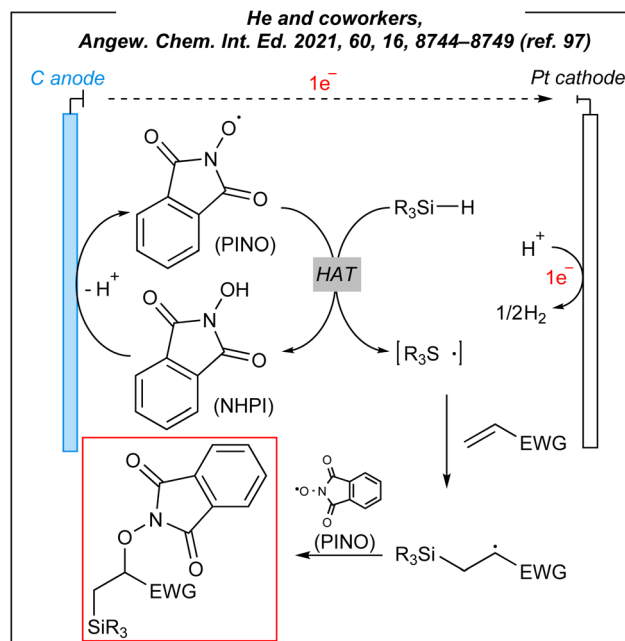


Fig. 11 Plausible mechanism for the 1,2-silylfunctionalization.

should be favoured. As the result, the PINO radical abstracts the hydrogen atom from the Si–H bond of hydrosilanes. The formed silyl radicals are subsequently added to the alkene substrate giving silyl alkyl radical, which is followed by the radical–radical coupling between the latter ones with *N*-oxyl species to give 1,2-silyl-oxygenation products (Fig. 11).

To sum up, He and coworkers reported a novel methodology for the silyl-oxygenation of activated alkenes, induced by electricity. First of all, the authors used hydrosilanes as the substrates, which is a typical choice for this type of reaction. However, usually, the scope of hydrosilane is limited to triethylsilane or tris(trimethylsilyl)silane, and the conversion of Si–H moieties requires the use of stoichiometric peroxides, traditional transition-metal catalysis or metallaphotocatalysis.^{98–107} Despite some disadvantages, the mentioned approaches are more or less a sustainable way to obtain the desired 1,2-silylfunctionalized products. Here, He's method stands out from others in terms of a wide range of silicon substrates. Furthermore, the electrochemical system consists of a graphite anode and a platinum cathode. The latter is classified as an expensive electrode but also reusable. Similarly to Lin⁶⁵ and Zhang,⁸⁶ He and coworkers again used an IKA® ElectraSyn 2.0, which ensures the reproducibility of the obtained results. In conclusion, the electrochemical 1,2-silylfunctionalization of alkenes reported by He and coworkers is an interesting alternative to other synthetic methods. Despite some limitations in the alkene scope, it can be considered a useful synthetic approach.

In 2021, Han and Jing achieved the synthesis of dibenzosiloles through electrocatalytic sila-Friedel-Crafts reaction.¹⁰⁸ For this process (Fig. 12), the authors used the following combination: RVC anode, platinum cathode, CCE @ 5 mA, NHPI





Fig. 12 Electroinduced sila-Friedel-Crafts reaction leading to dibenzosiloles.

as HAT mediator (1.2 eq.), pyridine as an additive (2.0 eq.) and $n\text{Bu}_4\text{NPF}_6$ as the electrolyte. During the optimization studies, several HAT mediators were tested including NHPI (selected), NHSI, quinuclidine, and DABCO. The mediator-free attempt was also carried out and proved the essential role of the HAT-step. Han also demonstrated the necessity of electricity, and that pyridine was the additive of choice. After considerable experimentation, it was also found that $\text{CH}_3\text{CN}/\text{HFIP}$ mixture (50:1) is crucial, and the absence of HFIP (hexafluoroisopropanol) gave inferior results. Upon the investigation of the reaction scope, it was revealed that biaryl-2-yl-diphenylsilanes with both electron-donating groups and electron-withdrawing substituents at the phenyl rings are compatible with the process

conditions, leading to the desired products in moderate to excellent yields (32–96%).

However, in the vast majority of cases, the substrates with activated rings afforded higher yields. It is worth noting that the nature of substituents at silicon atoms is crucial, probably due to stabilization effects. Thus, the best results were obtained for biaryl-2-yl-diphenylsilanes, whilst biaryl-2-yl-methylphenylsilane and biaryl-2-yl-dimethylsilane gave inferior results (62% and 36%, respectively).

The presented reaction system involved a HAT mediator – NHPI, which undergoes deprotonation facilitated by pyridine, and a subsequent anodic oxidation process. As the result, the PINO radical is afforded and it abstracts the hydrogen atom from the Si–H bond of hydrosilane. The formed silyl radical is subsequently oxidized to a silyl cation. The formation of R_3Si^+ species was indirectly confirmed by quenching the cations with water to afford the corresponding silanols (similar to Zhang's procedure). However, under standard conditions, the silyl cations cyclize through sila-Friedel-Crafts reaction. The plausible mechanism is depicted in Fig. 13.

To sum up, Han and coworkers reported a novel methodology for the synthesis of dibenzosiloles, induced by electricity. The reaction proceeds *via* cyclization of *in situ* generated silyl cations (*via* sequence: hydrosilane – silyl radical – silyl cation).

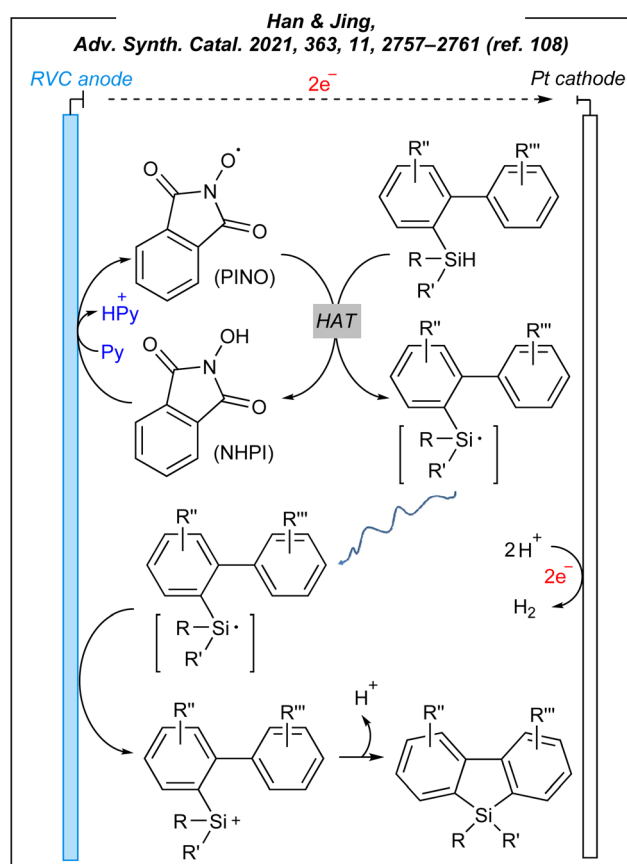


Fig. 13 Plausible mechanism for the electrocatalytic sila-Friedel-Crafts reaction.



The SiH-substituted biaryls are a typical choice for this type of reaction. The authors showed that triarylsilanes give the best results, with a wide range of substituents at biaryl rings. To date, there were four major ways to obtain dibenzosiloles. The conventional coupling between readily available chlorosilane with organometallic derivative has a limited scope and gives the desired products with low yields.^{109,110} Secondly, there are radical approaches usually suffering from harsh conditions and stoichiometric amounts of oxidants.^{111,112} There are also classical dehydrogenative coupling processes employing very expensive transition metal complexes (such as Rh).^{113–115} Finally, the sila-Friedel-Crafts reactions can be performed in the presence of trityl cation¹¹⁶ or cationic Ru-S complexes.^{117,118} Thus, from the synthetic point of view, the electrochemical approach seems to be a sustainable alternative to known procedures (*e.g.*, no TM-catalysts, no external oxidants, *etc.*) Furthermore, the electrochemical system consists of an inexpensive graphite anode and an expensive platinum cathode. The authors used a homemade reactor providing no crucial information about the anode dimensions and the current density. In conclusion, the electrochemical sila-Friedel-Crafts reaction reported by Han and coworkers is an interesting alternative to known synthetic protocols, but it has some limitations in the scope (*e.g.*, mostly the utilization of triarylsilyl derivatives) and supporting information for the users.

Recently, Poisson and coworkers disclosed a novel strategy to carry out hydrosilylation reaction by using the Suginome reagent (PhMe₂Si-Bpin) and alkynes under electrochemical conditions (Fig. 14).¹¹⁹

This article clearly shows how important recent developments in the field were. For the formal hydrosilylation process, the authors used the following combination: stainless steel electrodes (both anode and cathode), CCE @ 10 mA, and *n*Bu₄NCl as the electrolyte. Control experiments showed that a mixture of CH₃CN/CH₃OH (9:1) is crucial to obtain the desired products, and the essential role of electricity was also confirmed. The switch from *n*Bu₄NCl to *n*Bu₄NBF₄ led to lower conversion but slightly better selectivity. Subsequently, the authors investigated the scope of this hydrosilylation approach. A wide range of phenylacetylene derivatives worked efficiently under the reaction conditions. Furthermore, commercial ene-yne derivative also participated effectively in this process, while preserving the ene-functionality untouched. Finally, the authors were able to convert a few biorelevant complex molecules, as well as four internal alkynes.

To gain some mechanistic insights into this electroinduced transformation, the authors conducted some experiments. Firstly, the origin of the hydrogen atom (red colour in Fig. 14) added to the vinyl radicals was examined. Unlike Lin, and despite a lower bond dissociation energy of the C–H bond in CH₃CN molecule, Poisson proposed that CH₃OH serves as the hydrogen source (not CH₃CN). It was confirmed *via* labeling experiments; however, the true nature of this process is still unknown. The plausible mechanism is depicted in Fig. 15.

It assumes, that firstly, the methoxide anion reacts with the Suginome reagent to form anionic borate species, which is fol-

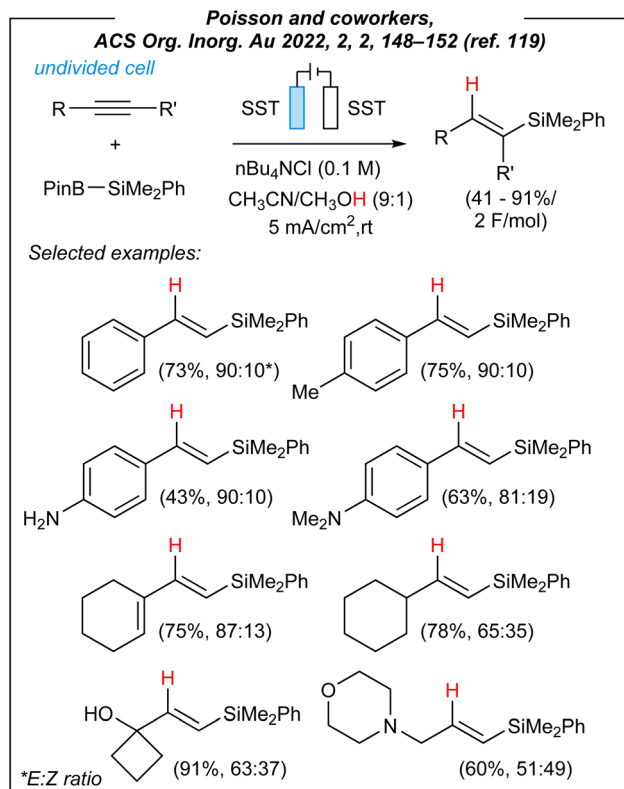


Fig. 14 Hydrosilylation of alkynes under electrochemical conditions.

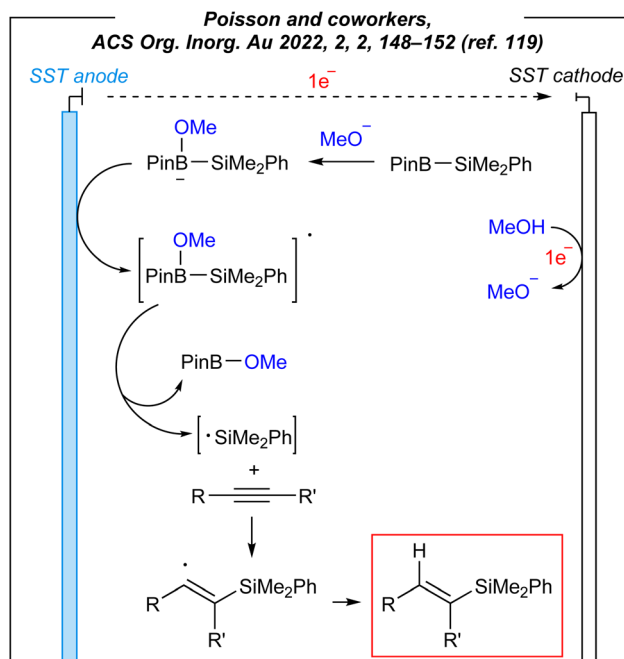


Fig. 15 Plausible mechanism for the electroinduced hydrosilylation.

lowed by the anodic oxidation of the latter to form borate radical species. Their decomposition leads to methoxyboronic acid pinacol ester and silyl radicals. The next step involves a



Highlight

nucleophilic silyl radical addition to the alkyne to generate a Si–C bond. The highly reactive vinyl radicals undergo the radical–radical coupling or they abstract the proton from tetra-coordinated boron species (formed from methanol and Suginome reagent).

To sum up, Poisson and coworkers reported a novel methodology for the hydrosilylation of alkynes, induced by electricity. First of all, the authors used only Suginome reagent as the source of silicon (it is worth noting, that recently, the authors disclosed also another interesting application of this compound under electrochemical conditions¹²⁰). The mentioned 2-(dimethylphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane is commercially available but quite expensive (Merck – 104€ per 1 g; Gelest – 462.00\$ per 2.5 g). The future expansion of the scope (for other B–Si species) would imply an additional preparation of such precursors. Fortunately, the scope of alkynes includes a wide range of terminal and internal derivatives, giving access to several hydrosilylation products. Of course, there are plenty of methods to achieve Si–H addition to unsaturated bonds.^{34,121–123} However, they involve the use of radical generators or different catalysts (mainly TM-complexes). Therefore, a very important step is searching for an alternative to highly expensive oxidants, as well as catalysts based on platinum or rhodium.^{124–129} Furthermore, in terms of the electrochemical system, the authors used readily available stainless steel electrodes. Similarly to Lin,⁶⁵ Zhang,⁸⁶ and He,⁹⁷ also Poisson and coworkers used an IKA® ElectraSyn 2.0, which ensures the reproducibility of the obtained results. In conclusion, the presented electrochemical hydrosilylation of alkynes is a fresh look at the process of Si–H addition to unsaturated bonds. Despite some limitations (*e.g.*, all reactions limited to the Suginome reagent, the mixture of *E/Z* isomers, *etc.*), it can be considered as one of the pioneering achievements, which should stimulate further development of this field.

The main goal of this perspective was to showcase the diverse synthetic approaches associated with the electroinduced cleavage of Si–H, Si–Cl, and Si–B bonds enabling the synthesis of several organosilicon compounds. These, in turn, create a platform for both known and completely new materials. During the last two years, a significant recent impetus has been gained by the use of electrosynthesis. Notably, this also involved the use of knowledge regarding previous investigations dating back to the 1970s. The major advances had been achieved with the reproducibility and accessibility of the electrochemical approaches. Commercial, standardized equipment such as IKA® ElectraSyn 2.0 may revolutionize the electrochemical synthesis itself. Given the importance of organosilicon compounds for material chemistry, further exciting advances are expected in this constantly-evolving research area. These should address the use of less expensive precursors and additives, the issue of selectivity, and probably the development of electrocatalytic approaches for more challenging transformations. Finally, it is hoped that further achievements will meet the criteria of broadly understood green synthesis, which will ensure the sustainable development of our societies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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